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6. AUTHOR(S)

Dr. Yurii V. Rud

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Russian Academy of Sciences
26 Polytekhnicheskaya
St Petersburg 194021
Russia

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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Russian Academy of Sciences as follows: Provide from ten to fifty specimens of cadmium germanium arsenide in four different geometries.

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Title: **New Infrared Laser Wavelength Conversion Materials**

Organization: A.F. Ioffe Physico-Technical Institute
26 Politechnicheskaya ul
Russia

Contributors: Yu. V. Rud'
B. H. Bairamov

Introduction

Crystals with the chalcopyrite-type structure belonging to I-IV-V_2 group can be considered to be a ternary analog of the III-V binary compound semiconductors. They are technologically important material and have attracted much attention due to their large nonlinear optical coefficients and birefringence. Their electronic structure are quite different from the binary analogs, and, hence, there is considerable interest in studying the structural, electrical and optical properties of these materials from fundamental as well as application point of view.

Objective

The principal purpose of this research project is to enhance the technology base of the growth processes by understanding crystalline structure and performing electron transport and optical measurements to obtain high quality crystals. The specific material of primary interest is cadmium germanium diarsenide crystals which are useful for infrared wavelength conversion.

Technical Approach

Technical approaches used for these objectives included considerable fundamental research and development as of the growth method based on a crystallization of cadmium germanium diarsenide single crystals from the stoichiometric solution of this compound as well as thermal annealing treatments.

A focused effort is made to develop structural characterization methods, such as Raman scattering, as well as Hall effect and conductivity measurements on oriented cadmium germanium diarsenide single crystals.

Results

This is a final report of the research program of integrated investigations of growth, electron transport and optical properties of cadmium germanium diarsenide single crystals.

We are making a systematic fundamental study of the growth parameters that lead to a high-quality cadmium germanium diarsenide single crystals.

1. Polycrystalline Cadmium Germanium Diarsenide Feed Materials Growth

In order to provide enough single-phase cadmium germanium diarsenide polycrystalline feed materials for further growth of single crystals we have performed several synthesis experiments by pre-reacting of preliminarily specially purified high quality cadmium, germanium and arsenic elements as starting materials yielding approximately 25 grams each.

2. Growth of Cadmium Germanium Diarsenide Single Crystals

In order to grow high optical quality cadmium germanium diarsenide single crystals we have employed the method of horizontal directional crystallization from the solution which was close to stoichiometric.

Polycrystalline starting materials were loaded into the graphitized quartz crucible which were inserted in an evacuated quartz tube. The temperature field gradient was approximately 2-3 degree/cm. The melted samples were kept at approximately 800 °C and then slowly cooled down to room temperature at the rate 20-40 °C/h.

As a result of crystallization spontaneous formation of single crystal were achieved which were separated and cut from the grown large scale bloc ingots. The reason of crack formation is not established yet and for its elimination hard stabilization is necessary.

3. Annealing

In order of further stabization of free carrier concentration and improving of optical absorption properties in the infrared range of the spectra the grown samples of cadmium germanium diarsenide single crystals were annealed at 500 °C, during 250-400 hours.

Annealing experiments were conducted under controlled vapor pressures of cadmium and arsenic in an effort to improve the process.

4. Study of Kinetic Properties of Orienred Cadmium Germanium Diarsenide Single Crystals

Cadmium germanium diarsenide single crystals in an ordered state have chalcopyrite structure with the largest tetragonal deformation along [001] direction $\tau = 0.151$ [1-3].

Theoretical estimations predict anisotropic effective mass: $m_c^{\perp}/m_c^{\parallel} = 1.30$ and $m_{vl}^{\perp}/m_{vl}^{\parallel} = 1.91$ [2]. Therefore it is possible to expect sharp anisotropy of the electrical conductivity [3,4].

The electrical conductivity σ and Hall coefficient R were measured for our undoped and electrically homogeneous samples. The samples were parallelepippeds (with average dimensions 10x2x1 mm^3) oriented along the principal crystallographyc axes [100] and [001] which allow us to determine both independent components of the tensors σ and R. Current contacts were formed by deposition of pure copper on the end surfaces of the parallelepipeds. The eight potential probes on the side surfaces were made by platinum wires, which were welded by an electric discharge.

The measurements were performed in a weak electric and magnetic fields by the four-probe method in a wide temperature rane 80 - 750 K.

The confimatory measurements of the Hall emf's $V_R^{\perp}$ and $V_R^{\parallel}$ were made on samples of both orientations as a function of the angle φ between the carrent $i^{\perp}$ (or $i^{\parallel}$) and the magnetic field. They showed that $V_R^{\perp}$ and $V_R^{\parallel}$ are proportional to $sin\varphi$ (Fig. 1) where symbols $\perp$ and $\parallel$ correspond to components of the tensors i, σ or R and relative teragonal c-axis. In the investigated rage of temeperatures the ratio of the Hall coefficients was $R^{\perp}/R^{\parallel} \approx 1$. Therefore, the spatial distribution of Hall coefficient is practically isotropic within the limits of the experimental error.

Figure 2 shows typical temperature dependencies of the two independent components of the tensors $\sigma(T)$ and $R(T)$. The analysis of these data show that in the range of temperatures T < 400 K all samples exibite extrinsic p-type conductivity. The activation energy derived for acceptor centers $E_a = 0.15$ eV.

The deviation of the dependencies $\sigma(T)$ and $R(T)$ from the exponential low , exibited by all crystals at T < 120 K could indicate a transition to the hopping conduction among impurities.

The main conclusions of these temperature dependencies are sa follows: The Hall coefficient is isotropic in the extrinsic and intrinsic regions. So it is possible to addopt the one-ellipsoid model for the upper

valence band and for the conduction band of the cadmium germanium diarsenide single crystals.

The observed temperature dependencies of the tensors $\sigma^{\parallel}$ and $\sigma^{\perp}$ are in good agreement with the nature of the effective mass anisotropy $\sigma^{\parallel} > \sigma^{\perp}$ and this behavior does not depend in the investigated samples on hole concentration (see Table 1).

Typical temperature dependencies for the independent componenets of the Hall mobility for our p - type cadmium germanium diarsenide single crystals are shown in Fig. 3. It is clear that the transport of carriers is carracterised by the predomonance of $u^{\parallel}$, compared with $u^{\perp}$, which is entirely due to the anisotropy of the electrical conductivity.

It is interesting to note that the obtained temperature dependencies of $u^{\parallel}$ and $u^{\perp}$ are similar. Therefore, we can conclude that in the extrinsic conduction region the mobility of holes is governed primarily by the competion between two scattering mechanisms: the scattering by static defects at temperatures below 180 K, and the scattering by lattice vibrations at temperatures above 240 K.

Figure 4 represents typical temperature dependens of the anisotropy of Hall mobilty $K = u^{\parallel}/u^{\perp}$. As one can see from the Table 1 that this parameter is practically independent on the hole concentration.

Finally, the discovery of the current-flow anisotropy of cadmium germanium diarsenide single crystals cannot be rulled out. It should be taken into acount in the interpretation of transport properties and should also help to improve the efficiency of the photoelectronic devices.

5. Study of Kinetic Properties of Termally Annealed Cadmium Germanium Diarsenide Single Crystals

Figure 5 and 6 show concentration dependencies of holes of cadmium germanium diarsenide single crystals on thermal treatment time in saturated arsenic and cadmium vapor, respectively.

Such a treatment in the arsenic vapor lead first in one group of the crystals to the increasing and in other group to the reducing and then incresasing with futher achieving of the equilibrium value at t > 200 h.

Suach a treatment in the cadmium vapor lead to the reducing of the initial hole concentration.

These results indicate direct evidence of the physical base of improvement of the optical transparency of cadmium germanium diarsenide single crystals by thermal treatment in controled conditions.

6. Experimental Observation of Raman Scattering by Optical Phonons on Oriented Cdmium Germanium Diarsenide Single Crystals

To chracterize the crystalline perfection and to study lattice vibrational properties of the grown cadmium germanium diarsenide single crystals we have performed Raman scattering measurements.

Until now, due to the difficulties with the detection of Raman signals in such a small band gap (E_g (0 K) = 0.75 eV) crystals these measurements have not been reported.

As an example Fig. 7 represents our polarised Raman spectra obtained at T = 300 K in backscattering geometry from the oriented (110) surface of the cadmium germanium diarsenide single crystals by using 514.5 nm line as an excitation source. Our preliminary results [8] show that the observed features are induced by long-wavelength Brillouin zone-center optical phonons. The sharpness of the lines with deconvoluated values of the full width at half intencity of 1 - 3 cm^{-1} as well as properly polarization behavior indicate on high crystalline quality of the grown samples.

First experimental observation of Raman scattering opens new possibilities for a direct measurements with a rather high degree of sensitivity of the crystalline perfection of cadmium germanium diarsenide single crystals.

Conclusions

As a result of these performed experiments we are able to report that :

- Single-phase of cadmium germanium diarsenide polycrystalline feed materials growth were conducted by pre-reacting the specially purified cadmium, germanium and arsenic elements.

- Cadmium germanium diarsenide single crystals were grown by horizontal direct crystallization method with the temperature field gradient of approximately 2-3 degree/cm. The melted samples were kept at approximately 800 °C and then slowly cooled down to a room temperature at the rate 20-40 °C/h.

- Annealing of cadmium germanium diarsenide single crystals were conducted at about 500°C, during 250-400 hours and under controlled vapor pressures of cadmium and arsenic.

- The electrical conductivity and Hall coefficient were measured for our undoped and electrically homogeneous samples and the anisotropy of current-flow anisotropy of cadmium germanium diarsenide single crystals was discovered which cannot be rulled out in the interpretation of their transport properties.

- Results of transport measurements of annealed samples indicate to the physical base of improvement of the optical transparency of cadmium germanium diarsenide single crystals.

- First experimental observation of Raman scattering demonstrate high crystalline quality of the grown samples and opens new possibilities for a direct measurements with a rather high degree of sensitivity of the crystalline perfection of cadmium germanium diarsenide single crystals.

Future Research

Future studies will focus on continuing to advance our understanding of how details of microstructure of the grown by horizontal direct crystallization determine its unusual optical and electrical properties and on extending our investigations to low temperature Raman and luminescence measurements of doped cadmium germanium diarsenide single crystals. These studies are important for better understanding and optimizing the high-quality cadmium germanium diarsenide single crystals growth as well asirradiation and thermal annealling treatments processes.

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Table 1.

Electrical properties of of oriented p-type cadmium germanium diarsenide single crystals at $T = 300$.

Samp. No.	$R^{\parallel}$	$R^{\perp}$	$u^{\parallel}$	$u^{\perp}$	$\sigma^{\parallel}$	$\sigma^{\perp}$	p	$K = u^{\parallel}/u^{\perp}$
	cm^3/C		$cm^2/V{\cdot}s$		$(\Omega{\cdot}cm)^{-1}$		cm^{-3}	
13	$2.10x10^4$	$2.05x10^4$	790	255	0.038	0.012	$3x10^{14}$	3.1
7	$3.10x10^3$	$3.10x10^3$	415	148	0.130	0.044	$2x10^{15}$	3.0
18	$3.10x10^3$	$3.10x10^3$	200	65	0.064	0.021	$2x10^{15}$	3.1
21	$2.10x10^3$	$2.15x10^3$	410	130	0.200	0.062	$3x10^{15}$	3.1
19	$1.60x10^3$	$1.60x10^3$	400	130	0.250	0.080	$4x10^{15}$	3.1
14	$3.10x10^2$	$3.15x10^2$	280	94	0.890	0.300	$2x10^{16}$	3.0
6	15.7	15.8	140	45	8.9	2.9	$4x10^{17}$	3.1

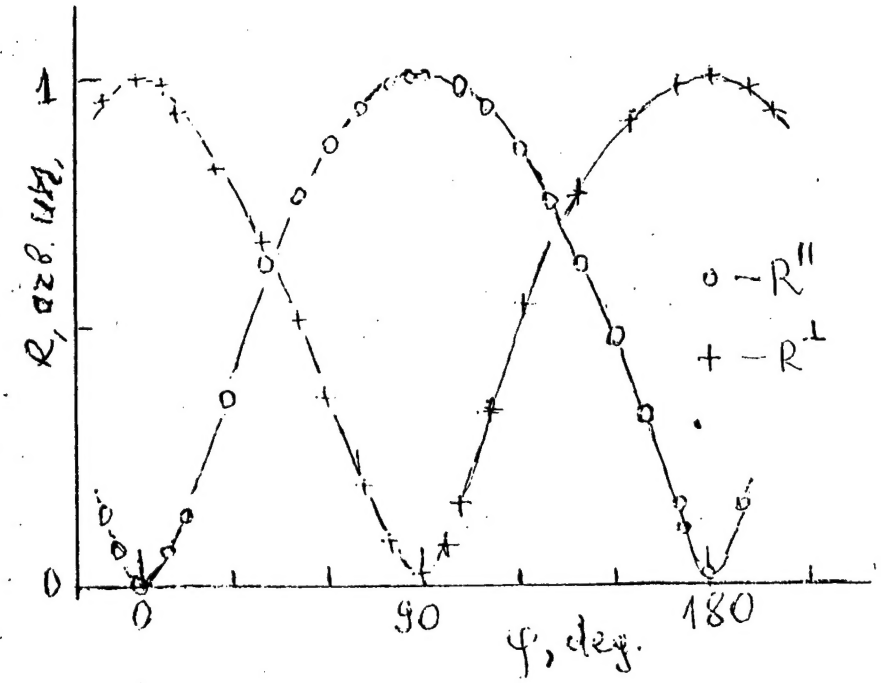

Fig. 1. Dependence of independent components of Hall coefficient tensor on angle φ - betwen the tetragonal axis c and direction of magnetic field H of oriented p-type cadmium germanium diarsenide single crystals at T = 300 K. ($\varphi = 0$ at $c \parallel H$ sample No.18).

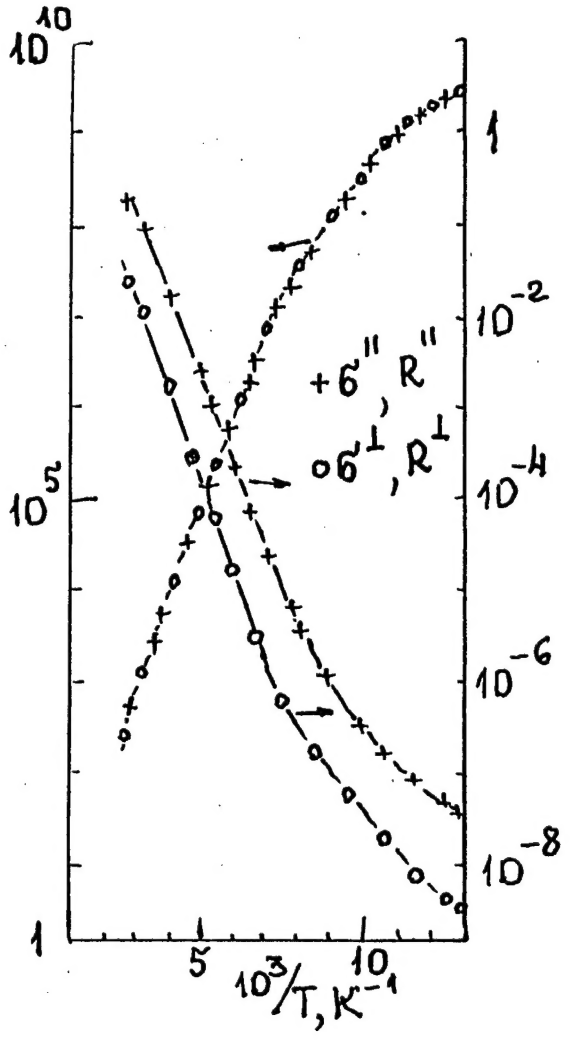

Fig. 2. Temperature dependence of conductivity and Hall coefficient of oriented p-type cadmium germanium diarsenide single crystals. (sample No.18, $H = 8$ kG).

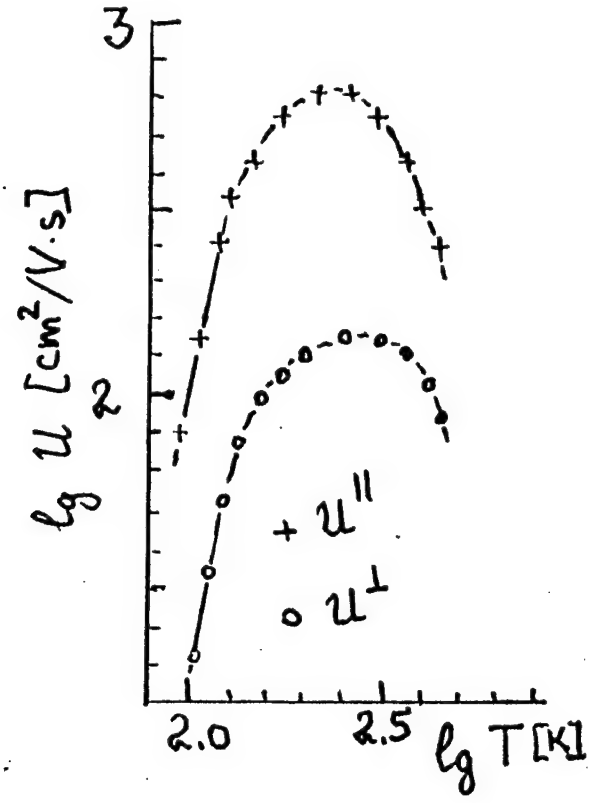

Fig. 3. Temperature dependence of independent components of Hall mobility's tensor of oriented p-type cadmium germanium diarsenide single crystals. (sample No.18).

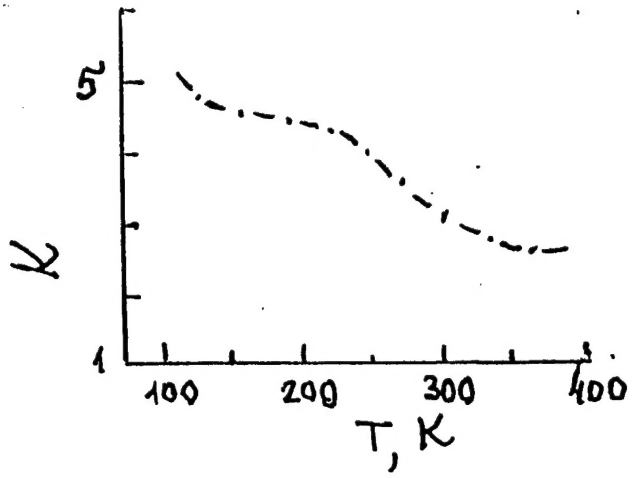

Fig. 4. Temperature dependence of anisotropy coefficient of Hall mobility of p-type cadmium germanium diarsenide single crystals. (sample No.18).

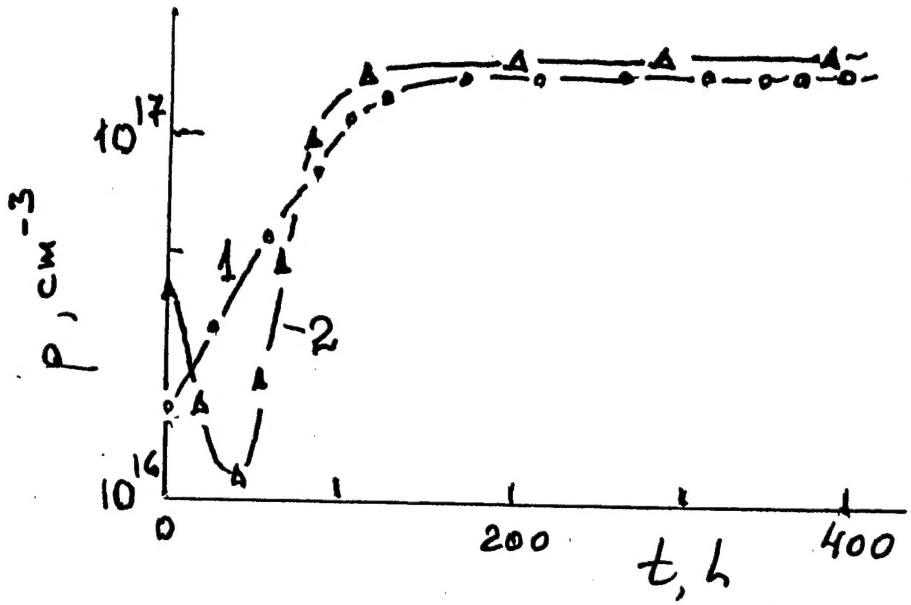

Fig. 5. Concentration dependence of holes of cadmium germanium diarsenide single crystals on thermal treatment time in saturated arsenic vapor. (Treatment temperature T = 450 °C, 1 - sample No. 5, 2 - sample No. 7).

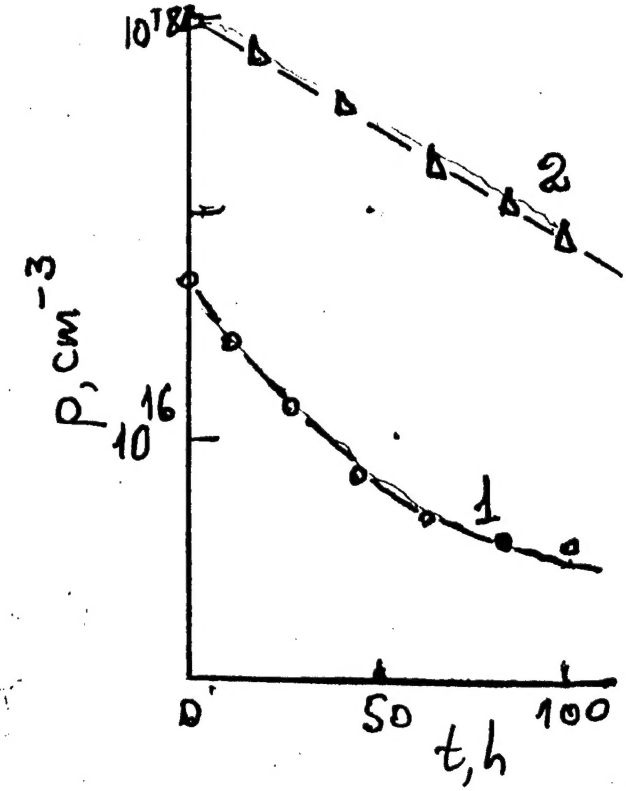

Fig. 6. Concentration dependence of holes of cadmium germanium diarsenide single crystals on thermal treatment time in saturated cadmium vapor. (Treatment temperature T = 400 °C, 1 - sample No. 3, 2 - sample No. 17).

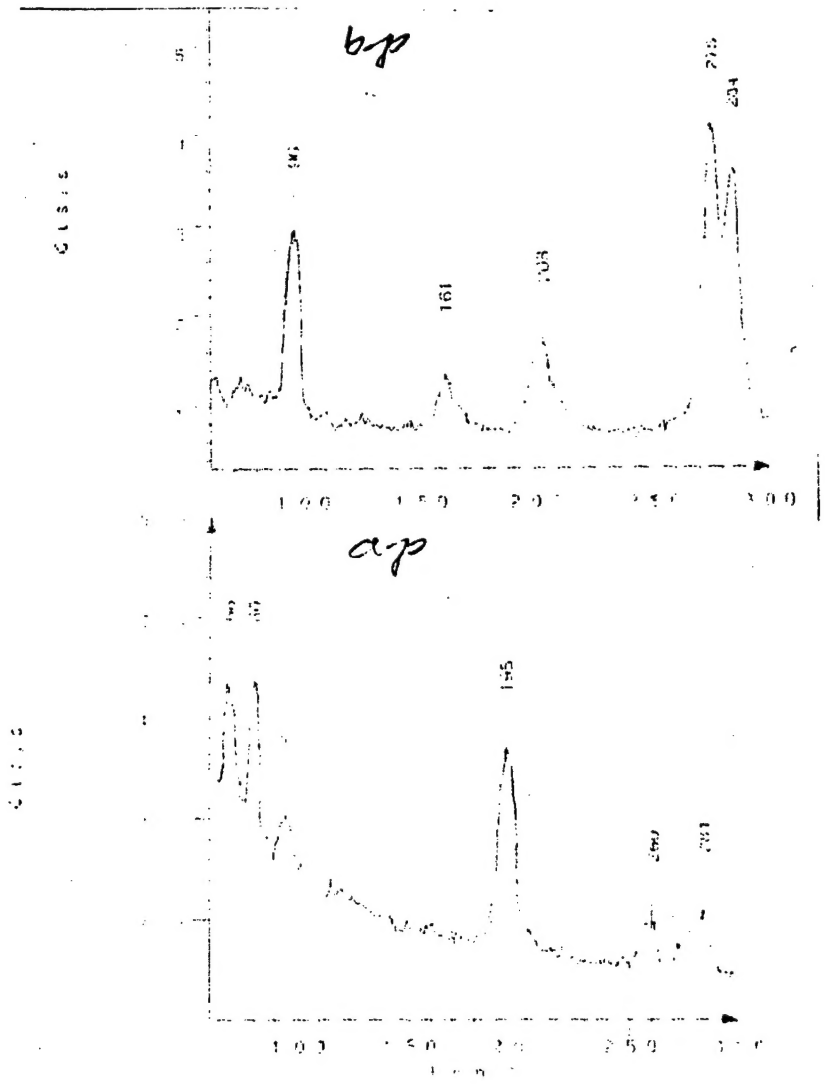

Fig. 7. Raman spectra of p-type cadmium germanium diarsenide single crystals obtained at backscattering gometries for the polarized (ad) and depolarized (bd) scattering with 514.5 nm line of an Ar+ - laser, 20 mW, T = 300 K.

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